

Watching GaN Nanowires Grow

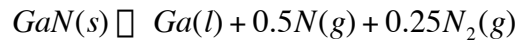
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Crucial to nanotechnology is the creation of nanoscale building blocks of various sizes and shapes.¹ Nanostructures of wide band-gap gallium nitride are of particular interest because of their applications in short-wavelength optoelectronic devices and high-power/high-temperature electronics. GaN nanowires represent unique building blocks that can be used as high mobility field effect transistors as well as miniaturized UV-blue nanolasers.^{2,3} The synthesis of GaN nanowires via the vapor-liquid-solid (VLS) process^{1,4} commonly relies on transition metal clusters such as Fe and Co, which inevitably results in undesired contamination within the otherwise single crystalline nanowires. Here we report real-time transmission electron microscopy (TEM) observations of the growth of GaN nanowires via a *self-catalytic* VLS mechanism. These nanowires nucleate and grow from Ga droplets formed during thermal decomposition of GaN at elevated temperatures in vacuum. This is the first direct observation of self-catalytic growth of nanowires via the VLS mechanism, and suggests new strategies for growth of semiconductor nanowires without unintentional doping.

The TEM samples studied in this work were pure GaN thin films grown to a thickness of 12 μm via hydride vapor phase epitaxy (HVPE) on the c-plane of sapphire.

The GaN film was subsequently removed from the sapphire substrate using the laser lift-off technique (LLO) to create a free-standing pure GaN layer.⁵ This free-standing layer was argon ion milled to electron transparency (≈ 300 nm thickness). The samples were then heated *in-situ* in a 200 kV transmission electron microscope to a temperature of $\sim 1050^\circ\text{C}$ at a vacuum level of $\sim 1 \times 10^{-7}$ torr. It is known that at temperatures above 850°C in high vacuum GaN decomposes via the following reaction:⁶



By heating the sample *in-situ*, it is possible to observe this decomposition and the resulting nanostructure evolution in real time and at high spatial resolution.

During this *in-situ* study, we serendipitously discovered the self-catalytic growth of GaN nanowires. In Figure 1, a series of video frames grabbed from observations of the GaN decomposition process at elevated temperatures are presented.⁷ The nucleation and growth of a single GaN nanowire from a Ga liquid droplet is outlined in these images. The initial decomposition of the GaN thin film results in isolated nanoscale Ga droplets, seen as dark spots in the TEM images (A). The decomposition of GaN also generates about 50% atomic nitrogen species as well as small percentage of congruent evaporated GaN species.⁶ These *vapor* species then re-dissolve into the Ga *liquid* droplets and initiate the VLS nanowire growth by supersaturating the liquid Ga and establishing a liquid-Ga/solid-GaN interface (B-F). The process resembles previous *in-situ* observations of Ge nanowire growth on Au clusters,⁸ where three stages, including alloying (Fig. 1A), nucleation (B) and axial growth (C-F), are readily resolved. The growth rate of these GaN nanowires, however, was estimated to be 300 nm/s, orders of magnitude faster than those of nanowires grown at high pressure (~ 300 nm/min) in a chemical vapor deposition

process.⁹ Significantly, the current GaN VLS nanowire growth proceeds in a self-catalytic fashion, avoiding potential contamination from any foreign metal atoms.

After the *in-situ* growth, the sample was cooled down and examined using conventional TEM methods at room temperature. In Figure 2(A), the sample is oriented close to the [0001] zone axis of the GaN substrate, where individual nanostructures of GaN can be observed. The selected area electron diffraction pattern (Fig. 2A inset) indicates that these nanostructures are indeed pure, single crystalline GaN. When the sample is tilted to approximately 30° away from the [0001] zone axis, we see that these islands are well-oriented GaN nanowire arrays with average diameters of around 50 nm.

Both the *in-situ* high temperature nanowire growth observation and room temperature examination of the products unambiguously demonstrate the feasibility of self-catalytic VLS nanowire growth, thus opening up the possibility of synthesizing electronically pure single crystalline semiconductor nanowires.

Figure Captions:

Figure 1. A series of video frames grabbed from observations of GaN decomposition at $\sim 1050^\circ\text{C}$, showing the real-time GaN nanowire growth process. The number on the bottom left corner of each frame is the time (second: millisecond).

Figure 2. Room temperature TEM images of GaN nanowire arrays observed nearly along the $[0001]$ zone axis (A) and 30 degrees away from the $[0001]$ zone axis (B). The inset in (A) is a selected area electron diffraction pattern recorded from the array, indicating that the islands are single crystalline GaN.

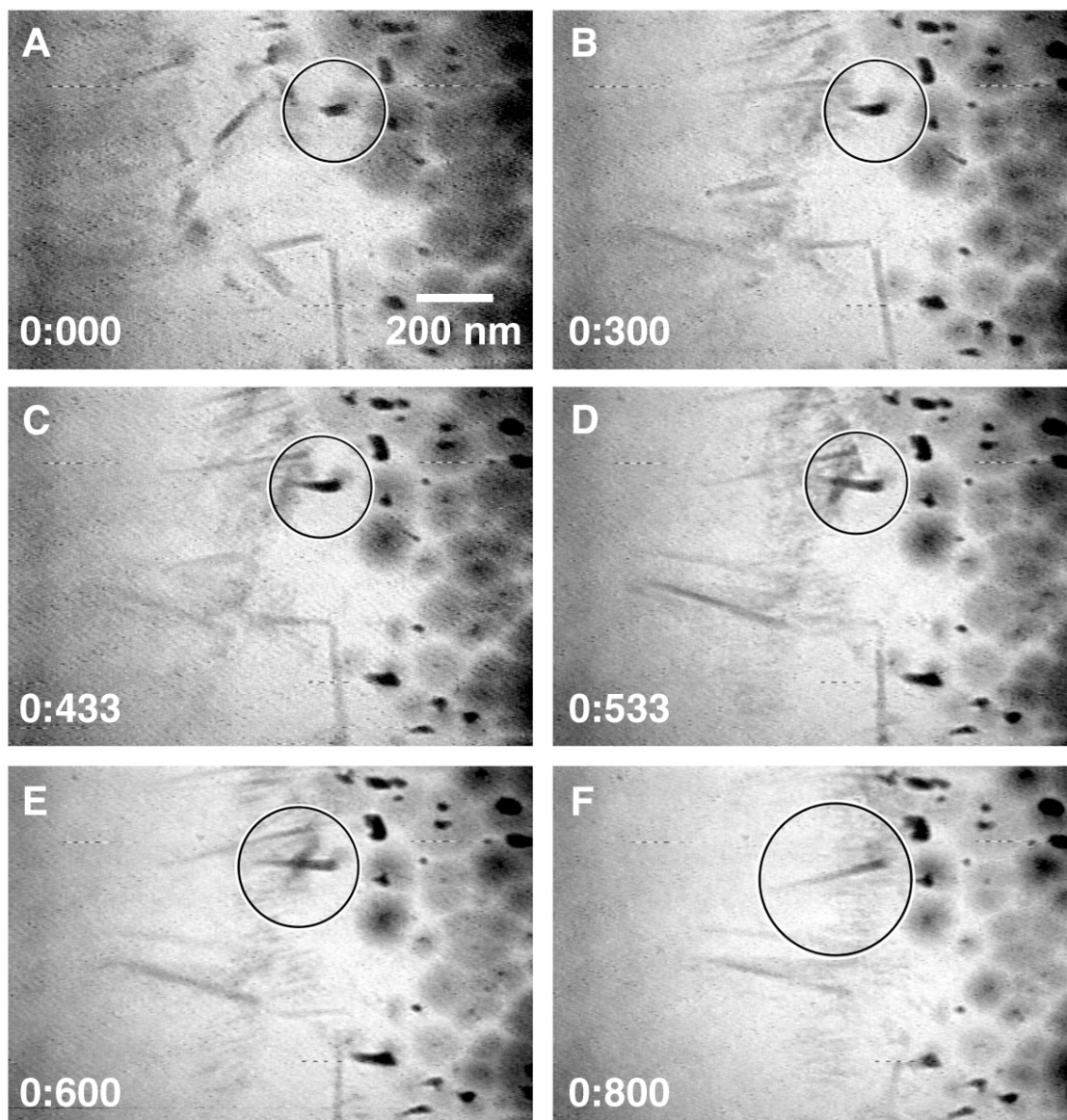


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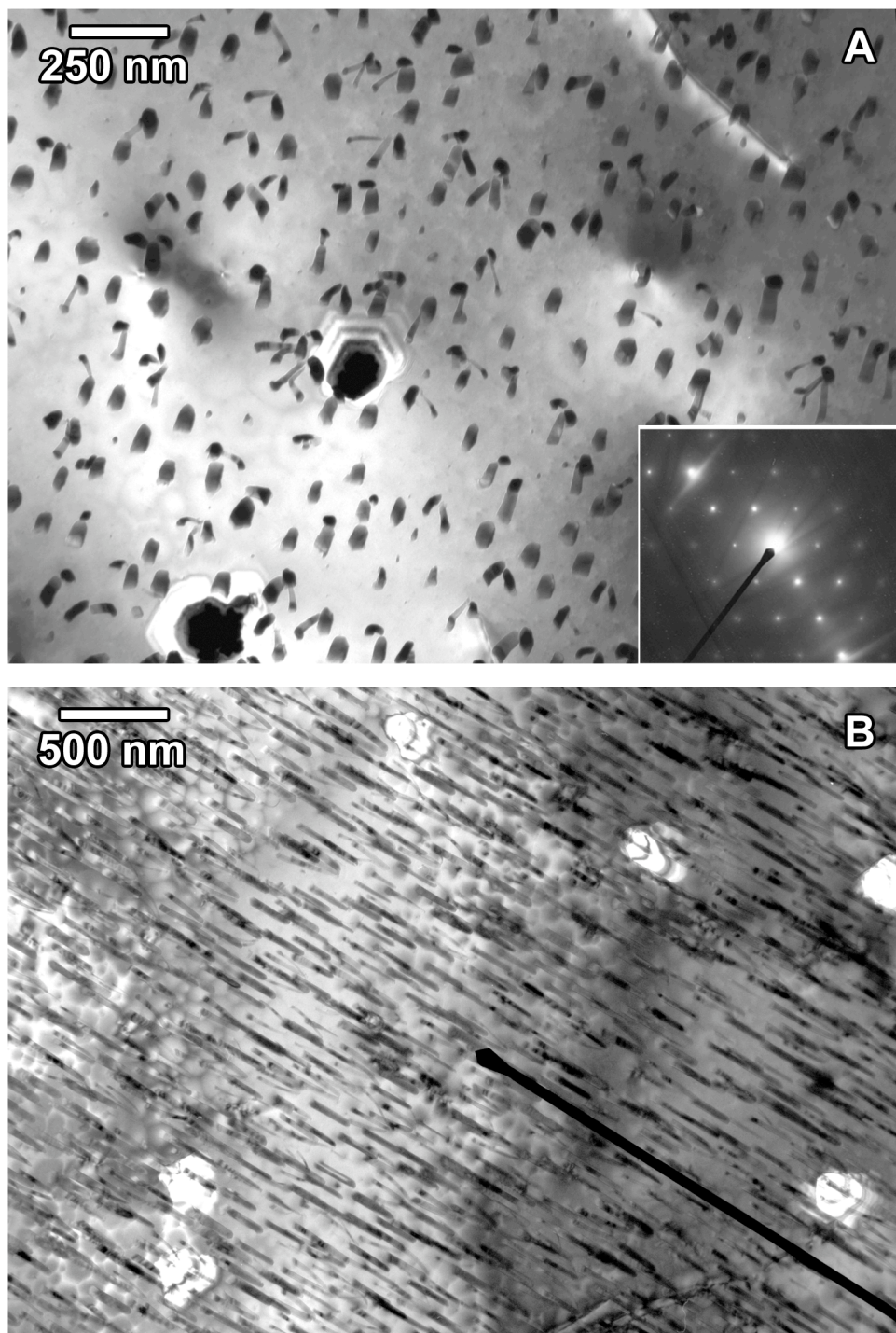


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- ¹⁰ The work at NCEM was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF000098. The author would like to thank J. Ren of AXT Corporation for providing the HVPE samples, W.S. Wong for the LLO preparation and T. Sands of Purdue University and C. Kisielowski of NCEM / LBNL for helpful discussions.